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## Specification

### 1. Title of the Invention

Method for Producing Polyvinyl Alcohol having Limited Range of Molecular Weight Distribution

### 2. Claims

A method for producing polyvinyl alcohol having a limited range of molecular weight distribution characterized by fractionation by subjecting granular, threadlike, or film-like polyvinyl alcohol to an immersion treatment in an aqueous solution of a salt heated to 70°C or more.

### 3. Detailed Description of the Invention

This invention relates to a method for producing polyvinyl alcohol (hereinafter abbreviated to PVA) having a limited range of molecular weight distribution. More specifically, this invention relates to a method for producing PVA having a limited range of molecular weight distribution to be used for a negative resist that is improved in resolution and corrosion resistance.

The technology of photo-etching of forming a protection film resistant to an activator on a specific part by photographic technology and eliminating the residual part by the activator has recently been utilized in various technical fields as a high precision processing method. Particularly,

the photo-etching technology is widely utilized in the field of electronics and considered important in productions of printed wirings, shadow masks for color televisions, integrated circuits, and the like. Properties required as the protection film (photoresist) resistant to the activator in the photo-etching technology include photosensitivity, adhesiveness to substrate, and the like, and, among others, resolution and corrosion resistance are most important due to the development of microscopic integrated circuits. A polycinnamic acid vinyl-based resist has been used for the production of integrated circuits, and its property of being unaffected by oxygen in the air during exposure has been of preference. However, the conventional polycinnamic acid vinyl-based resist has a drawback of poor corrosion resistance.

The inventors had filed a patent application based on the fact that polycinnamic acid vinyl of which a molecular weight distribution and a viscosity average polymerization degree are within specific ranges has excellent corrosion resistance and resolution.

Several methods have been known as a method for obtaining polycinnamic acid vinyl having a limited molecular weight distribution, and column fractionation of polycinnamic acid vinyl itself, PVA, or polyvinyl acetate, fractional precipitation, fractionation by way of gel permeation

chromatography (hereinafter abbreviated to GPC), special polymerization such as living polymerization, and the like have been known. However, all of these methods are not suitable as an industrial production method since the methods are complicated and entail a high cost. Therefore, as a result of extensive research, the inventors found that cinnamic acid esterification of PVA obtainable by an immersion treatment using a water-based solvent is truly suitable as an industrial production method for polycinnamic acid vinyl having a limited molecular weight distribution to thereby accomplish this invention.

That is, according to this invention, it is possible to obtain PVA having a limited range of molecular weight distribution by subjecting granular, threadlike, or film-like polyvinyl alcohol to an immersion treatment in an aqueous solution of a salt heated to 70°C or more, and, as a result, it is possible to suitably obtain polycinnamic acid vinyl having a limited molecular weight distribution by cinnamic acid esterification of thus-obtained PVA.

Fractionation of PVA by a solution process has been tried by Beresiewicz (J. Polymer Sci., 35, 321 (1958)) by way of extraction of a PVA thin film with water-containing n-propanol, but the fractionation was not successful due to crystallinity of PVA and strong hydrogen bond between hydrogen groups. The inventors found that it is possible to achieve the

fractionation by way of molecular weight without being influenced by the crystallinity and hydrogen bond by extracting PVA in a salt-water system at a high temperature.

PVA to be used in this invention is generally obtained by saponification of polyvinyl ester, and a saponification degree may preferably be 70 mol% at least, more preferably 85 mol% or more. Examples of the aqueous solution of salt to be used in this invention include aqueous solutions of salt such as sodium sulfate, potassium sulfate, ammonium sulfate, potassium carbonate, sodium carbonate, sodium chloride, potassium chloride, ammonium chloride, sodium citrate, sodium tartrate, and sodium hydrogenphosphate. A ratio between the salt and water is varied depending on the type of salt, saponification degree of PVA, and the like and may preferably be such a value that a yield of PVA to be obtained by the immersion treatment of PVA with the solution is 10% to 90%, preferably 30% to 80%. In the case of fractionating perfectly saponified PVA in a salt cake-water system, an amount of the salt cake suitable for satisfying the value is 10 to 17 (g/300 cc of water).

The temperature at which PVA is subjected to the immersion treatment using the mixture solution of the salt and water may preferably be 70°C or more, more preferably 80°C or more, and the immersion treatment may particularly preferably be performed at the boiling point of the mixture solution from

the view point of easiness of temperature control. The immersion treatment is performed by immersing PVA into the solution followed by stirring and the like, and a treatment time may preferably be one minute or more. A grain size, a thickness of a thread, and a thickness of a film of PVA may preferably be 10 mm or less from the practical point of view without particular limitation thereto.

As criteria for molecular weight distribution of PVA to be obtained in this invention, the molecular weight distribution is expressed by way of a ratio between a weight average polymerization degree ( $P_w$ ) and a number average polymerization degree ( $P_n$ ), and the molecular weight distribution is small when a value of the ratio is small. Ordinary PVA has  $P_w/P_n$  of about 2.0 to 3.0 based on the expression, but  $P_w/P_n$  of PVA to be obtained as an insoluble part by the method of this invention is 1.9 or less, though the value depends on the type of PVA to be used. As used herein, the ratio between the weight average polymerization degree and the number average polymerization degree was detected by a GPC measurement of a re-acetified substance of PVA. That is, the GPC measurement was performed by using GPC (model 200 manufactured by Waters) to which columns having nominal diameters of  $9 \times 10^5$ ,  $10^5$ ,  $3 \times 10^4$  and  $3 \times 10^3$  angstroms and charged with a crosslinked polystyrene gel were attached and in tetrahydrofuran. The polymerization degree was measured

by comparing an elution volume with that of polyvinyl acetate having a standard narrow distribution polymerization.

PVA having limited molecular weight distribution to be obtained by this invention becomes polycinnamic acid vinyl having limited molecular weight distribution by way of esterification with cinnamyl chloride in pyridine or alkali, for example. Thus-obtained polycinnamic acid vinyl is used as being dissolved together with a sensitizer and a stabilizer and particularly useful as a photoresist excellent in resolution and corrosion resistance in fine imaging technology such as integrated circuit production.

This invention will hereinafter be described more specifically in conjunction with example, but this invention is not restricted by the examples at all.

#### Examples 1 to 3

2 g of granular perfectly saponified PVA ( $P_w/P_n = 2.5$ ) having a viscosity average polymerization degree of about 2400 and a grain diameter of 120  $\mu$  or less was thrown into 800 cc of water containing a predetermined amount of a salt cake shown in Table 1 at 100°C, followed by stirring for a predetermined period of time. The supernatant was eliminated by inclination, and the precipitation was solidified with acetone to be collected and dried. Measurement of molecular weight distribution of PVA was performed by re-acetifying PVA and by way of GPC using tetrahydrofuran as a solvent. Measurement

of a polymerization degree was performed by way of a viscosity measurement of the re-acetified substance. Results are shown in Table 1.

(Table 1)

Example	Salt cake amount (g/800 cc of water)	Treatment time (hour)	Insoluble part		
			Yield (wt%)	Viscosity average polymerization degree	Pw/Pn
1	11.0	2.0	55	4250	1.71
2	12.0	0.5	74	3840	1.70
3	15.0	1.0	90	3490	1.77

As is apparent from (Table 1), it is possible to obtain PVA having a narrow molecular weight distribution and a high polymerization degree.

## Examples 4 to 9

Treatments were performed in the same manner as in Examples 1 to 3 using 2 g of granular PVA (Pw/Pn=2.6) having a viscosity average polymerization degree of about 1700.

Results are shown in Table 2. Grain diameters of PVA in Examples 4 to 7 and Examples 8 and 9 were 120  $\mu$  or less and 150  $\mu$  or less.

(Table 2)

Example	Saponification degree of PVA (mol%)	Salt cake amount (g/800 cc of water)	Treatment time (hour)	Insoluble part		
				Yield (wt%)	Viscosity average polymerization degree	Pw/Pn
4	100	13.5	0.5	80	2720	1.74
5	100	10.5	2.0	14	4220	1.81
6	98.5	15.0	2.0	85	2240	1.60
7	98.5	11.0	2.0	44	8270	1.72
8	89.0	10.0	2.0	76	2550	1.81
9	89.0	9.0	2.0	67	2650	1.76

It is apparent from (Table 2) that it is possible to obtain PVA having narrow molecular weight distribution even in the case where the polymerization degree and saponification degree of PVA to be used are varied.

#### Reference Example 1

0.5 g of PVA obtained in Example 4 was added to 25 cc of a dried pyridine and then maintained at 100°C for 8 hours or more, followed by cooling to a 50°C. 2.8 g of cinnamyl chloride was dissolved into 5 cc of methylethylketone and dripped, followed by stirring at 50°C for 6 hours. The reaction solution was diluted with 25 cc of acetone and filtered, and the filtrate was thrown into a large amount of water to precipitate a polymer. The precipitate was washed with methanol and dissolved into methylethylketone, and the polymer was thrown into water for reprecipitation purification, followed by drying. A yield was 1.55 g. A cinnamic acid esterification degree of PVA measured by element analysis was about 100%. Thus-obtained polycinnamic acid vinyl was dissolved into methylcellosolve acetate together with 5-nitroacenaphthene and hydroquinone to obtain a resist solution, and a silicon wafer of which a surface was oxidized was coated with the resist solution by rotation coating by a spinner, followed by exposure, development and etching. Properties as a resist for integrated circuit production were



evaluated to show considerably good resolution and corrosion resistance.